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High-resolution electronic spectroscopy of a nonlinear carbon chain radical $C_6H_4^+$

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A high-resolution gas-phase spectrum of a molecular absorption band around 604 nm is assigned as due to an electronic transition of a nonlinear $C_6H_4^+$ planar species starting from its $^2A''$ electronic ground state. The spectrum is observed in direct absorption by cavity ringdown spectroscopy through a supersonic planar discharge through a mixture of acetylene in helium. The spectrum has a clear rotational and *K*-type structure. This allows an accurate determination of the *B* and *C* rotational constants and an estimate for the *A* rotational constant in ground and electronically excited states. The resolved spectrum of the fully deuterated species $C_6D_4^+$ has been obtained as well. The results are compared both to the outcome of *ab initio* geometry optimizations and low-resolution absorption spectra in 6 K neon matrices obtained after mass-selective deposition. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1575736]

I. INTRODUCTION

In recent years many experimental studies have been reported presenting high-resolution spectra of pure and highly unsaturated carbon chain radicals. Microwave,[1] infrared,[2] and UV–VIS spectra[3,4] are available both from matrix and gas-phase studies, all of them having in common that the major part of the observed geometries is linear. Even for very long chains, such as $HC_{22}H$ (Ref. 5) and $HC_{17}N$ (Ref. 6), linear structures have been found. Theoretical studies, however, predict for longer chains cyclic structures as well.[7] In the case of C_{13}, for example, theory[8] predicts a cyclic ground-state structure, but the experimentally observed IR spectrum is clearly that of a linear chain.[9] A reason for this discrepancy might be simply that the experimental techniques—supersonic jet expansions or matrix deposition experiments—favor the production of linear species, because large-amplitude bending motions (that are necessary to close the ring) are frozen in the production process. A similar situation might apply to the interstellar medium, where many linear carbon chain species already have been identified and the number of cyclic structures is still rather limited.[10]

In this work the electronic spectrum of a member of a so-far-unstudied class of carbon chain radicals is presented: a nonlinear and noncyclic species. The spectrum was observed more or less accidentally around 604 nm when scanning for coincidences with diffuse interstellar band features in a hydrocarbon plasma. The observed spectrum has a clear rotational and *K*-type structure. Simulation of the spectrum allows an accurate determination of the molecular constants of the carrier. Study of the partially and completely deuterated species gives information on the number of (equivalent) hydrogen atoms. Final identification becomes possible following semiempirical and *ab initio* geometry optimizations for a number of species. These indicate that the band at 604 nm is due to the carbon chain cation $C_6H_4^+$ with a nonlinear $H–C{\equiv}C–C{\equiv}C–CH{=}CH_2^+$ planar molecular geometry. This is confirmed by the observation of their transition in the absorption spectrum obtained after mass-selective deposition of $C_6H_4^+$ ions generated in a hydrocarbon plasma in a 6 K neon matrix.

Spectroscopic data for species of the form $C_6H_4^{(+)}$ are so far missing. Only a photodissociation study has been reported in which $C_6H_4^+$ was generated following a ring opening reaction in cyanobenzene.[11] In the latter study geometry optimizations are reported using MNDO calculations, which result in a series of equilibrium structures for the cation in which the heat formation of the possible acyclic structures is about 150 kJ mol^{-1} lower than that of benzene-type structures. Among these is a geometry that is confirmed in the present study, a linear noncyclic structure that is very close to the geometry proposed for the neutral species: 1-hexene-3,5-diyne.[12,13]

II. EXPERIMENT

The experimental method has been described and uses cavity ringdown (CRD) spectrometer sampling a supersonic planar plasma.[14] The plasma is generated by a discharge through a gas pulse (−300 V, 30 Hz repetition rate) of a 0.5% C_2H_2 (and/or C_2D_2) in He mixture with a backing pressure of 10 bars in the throat of a 3 cm×100 μm multilayer slit nozzle geometry. Rotational temperatures of the order of 20–40 K are routinely achieved. The nozzle is mounted in an optical cavity where the expansion is intersected approximately 2 mm downstream by the pulsed light of a tunable dye laser (resolution 0.15 cm^{-1}). The light leaking out of the cavity is detected with a photodiode, and the resulting ringdown event is used as input for a standard ringdown

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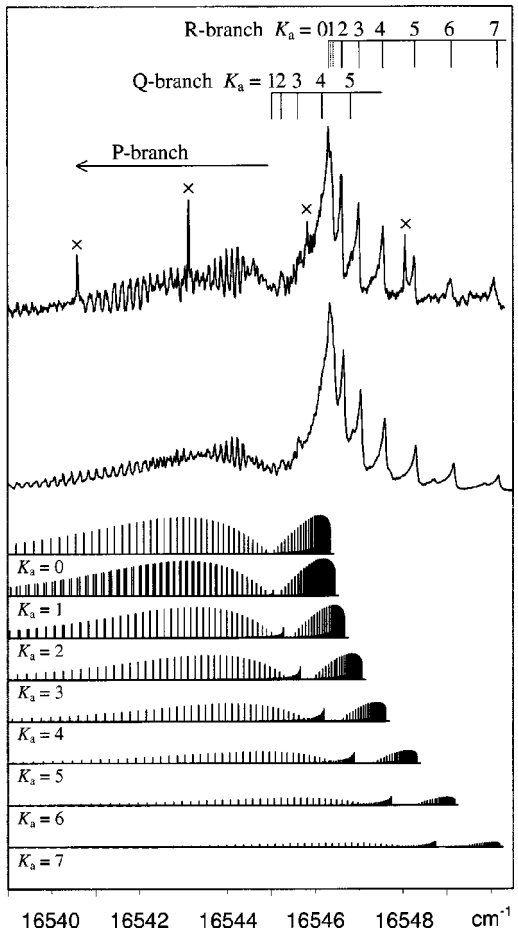

FIG. 1. Band observed at 604 nm using CRD spectroscopy through a supersonic planar plasma expansion. The rotational and *K*-type structure that is observed experimentally (top trace) can be simulated with a rotational temperature of 40 K, using constants derived from geometry optimizations for the nonlinear planar and noncyclic $C_6H_4^+$ carbon chain cation (second trace). The assignment is indicated in the figure and further illustrated by stick diagrams of each individual K_a. Lines marked with × are due to another carrier.

analysis.[15] A spectrum is recorded by determining an averaged ringdown time as a function of the laser frequency and calibrated by simultaneously recording an iodine spectrum.

III. RESULTS AND DISCUSSION

The CRD gas-phase spectrum of the band around 604 nm is shown in Fig. 1. A series of overlapping rotational transitions is observed as well as a *K*-type structure ($K=0-7$), typical for a nonlinear species. Using C_2D_2 instead of C_2H_2 yields a 67 cm^{-1} blueshifted spectrum with nearly identical spectral features, as shown in Fig. 2. This indicates that the carrier is of the form C_nH_m or $C_nH_m^{+/-}$.[16] In order to determine the values for *n* and *m*, a C_2H_2/C_2D_2 mixture has been used. A low-resolution scan, in which mainly the strong peaks for $K=0$ and 1 will be visible, gives five broadbands including bands originating from fully H- (16 546 cm^{-1}) and fully D- (16 613 cm^{-1}) substituted species. Three remaining bands located at 16 500 cm^{-1} (a), 16 560 cm^{-1} (b), and 16 595 cm^{-1} (c) are due to partially deuterated species. From this it can be concluded that $m=4$: the *a*, *b*, and *c* bands correspond to species with one, two, and three D atoms, respectively. The one-, two-, and threefold-deuterated species should have four, six, and four peaks by statistical arguments, but three, four, and three peaks are observed. This indicates that two of the four hydrogen atoms are rather similar.

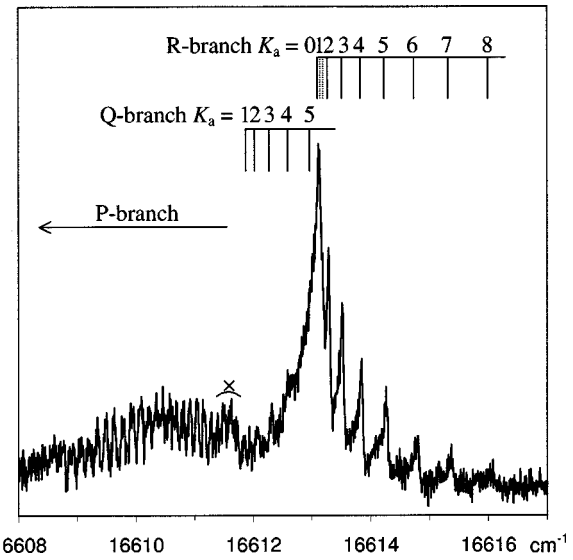

FIG. 2. Spectrum for the fully deuterated $C_6D_4^+$ species, blueshifted by approximately 67 cm^{-1} with respect to the $C_6H_4^+$ cation. Lines marked with × are due to another carrier.

The rotational analysis of the spectra with C_2H_2 and C_2D_2 as precursors allows the determination of the number of carbon atoms (n) in the chain. The stick diagrams (Fig. 1) show how the observed spectrum can be dissected into rotational transitions belonging to individual *K* values. The *P* branch consists of a series of transitions that are closely overlapping, causing some fluctuations in overall intensity, but which give a good indication for the value of B'' (C''). The change in rotational constants upon electronic excitation is reflected by a change of line distances, particularly for higher *J* levels on the *P* branch and gives values for B' (C'). The *R*-branch region consists of a series of unresolved bands with clear bandheads corresponding to $K=0-7$ as indicated in Fig. 1. The distance between the bandheads is a good indication for the value $\Delta A-\Delta B=(A''-A')-(B''-B')$, and the intensity ratio can be used to estimate A''. The *Q*-branch bands are rather weak and cannot be assigned directly. The overall pattern indicates a rotational temperature of the order of 40(5) K.

The spectra of $C_nH_4^{(+)}$ ($C_nD_4^{(+)}$) can now be rather well reproduced with rotational *B* and *C* constants of the order of 0.045 cm^{-1} (0.040 cm^{-1}) and an *A* constant of approximately 1.2 cm^{-1} (0.9 cm^{-1}) using WANG.[17] In view of the available constants for different kinds of carbon chain radicals determined in previous studies[18–20] this makes it very likely that $n=6$ or 7. Therefore possible equilibrium structures have been calculated for isomers of $C_6H_4^{(+)}$ and $C_7H_4^{(+)}$ (and fully deuterated isotopes) using MOPAC (Ref. 21) (PM3/UHF). The structure that gets closest to the observations is that of the nonlinear chain $H-C\equiv C-C\equiv C-CH=CH_2^+$ (Fig. 3) for which $A''=1.230$ cm^{-1}, $B''=0.0465$ cm^{-1}, and $C''=0.0448$ cm^{-1}. This struc-

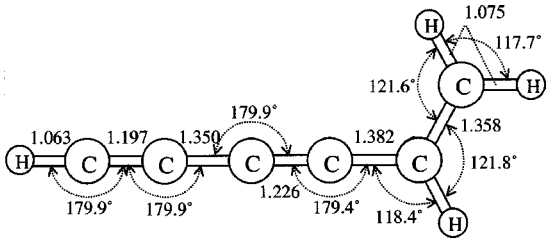

FIG. 3. Optimized molecular structure of $C_6H_4^+$ using *ab initio* calculations. The bond lengths are given in Å.

ture corresponds to one of the geometries calculated in Ref. 11 and is close to the previously proposed geometry of the neutral C_6H_4. Other isomeric structures yield sets of substantially different constants, particularly for the fully deuterated species, whereas the corresponding D–C≡C–C≡C–CD═CD_2^+ gives $A''=0.889$ cm^{-1}, $B''=0.0414$ cm^{-1}, and $C''=0.0395$ cm^{-1}, close to the simulated values for the spectrum observed here.

In order to improve the geometry optimization *ab initio* calculations have been performed using GAMESS.[22] In previous work ROHF/6-31G** calculations have been reported on the isomerization of C_4H_4 radical cations.[23] An identical method is applied here to $C_6H_4^+$. Rotational constants of $C_6H_4^+$ were determined using the *ab initio* optimized structure with bond lengths and angles as indicated in Fig. 3. The resulting constants are summarized in Table I and are close to the MOPAC results, as may be expected. The simulated spectrum, using the *ab initio* results, is plotted in Fig. 1 both as stick diagrams for individual K values and as an overall spectrum with an assumed resolution of 0.05 cm^{-1}. The calculated and observed spectra match very well apart from minor intensity deviations and a few lines that may belong to another carrier.

At this stage, however, two points remain unclear. First, it is not possible to discriminate between the neutral and cationic species from the rotational analysis alone. However, the neutral C_6H_4 is a closed-shell system and as a consequence it is unlikely that a strong electronic band is found at a rather low energy of 604 nm. In this case electronic transitions are expected in the UV. Indeed, the experimental conditions are in favor of a charged species. Second, it is not clear whether the band observed here is the origin band or a band that involves excitation of a vibrational mode in the upper electronic state—even though such bands are generally rather weak;[3] i.e., the origin band may be redshifted by a few thousands cm^{-1}. The change in rotational constants upon electronic excitation is minor and reflects a small elongation of the molecule in the upper electronic state. It is hard to conclude from these values that no vibrational excitation is involved. However, the present band is close to the well-studied and closely related $A\ ^2\Pi_g - X\ ^2\Pi_u$ electronic origin band transition of the linear triacetylene cation ($C_6H_2^+$) that has been located at 600 nm.[24] In analogy with the latter system, which is due to a transition from a $\cdots\pi_g^4\pi_u^3$ to a $\cdots\pi_g^3\pi_u^4$ configuration, it is very likely that the upper state of the observed band of the nonlinear $C_6H_4^+$ will have $^2A''$ symmetry. In this case the origin band of $C_6H_4^+$ is expected to be rather close to that of $C_6H_2^+$, as is observed.

TABLE I. Observed and calculated molecular constants of $C_6H_4^+$ and $C_6D_4^+$.

	$C_6H_4^+$		$C_6D_4^+$	
	Obs.[a]	*Ab initio*[b]	Obs.[a]	*Ab initio*[b]
A''	1.24	1.217	0.89	0.889
B''	0.0467	0.0471	0.0416	0.0420
C''	0.0449	0.0453	0.0400	0.0401
$A'-A''$	0.0767		0.0450	
B'	0.0452		0.0403	
C'	0.0434		0.0387	
$(A'-A'')-(B'-B'')$[c]	0.0782		0.0463	
T_{00}	16 544.980		16 611.91	

[a]Expected errors of the rotational constants are 0.1 cm^{-1} in A and 0.001 cm^{-1} in B and C, whereas 0.0006 cm^{-1} and 0.001 cm^{-1} for $B-C$ and $(A'-A'')-(B'-B'')$. Expected errors of T_{00} are 0.01 cm^{-1} for $C_6H_4^+$ and 0.1 cm^{-1} for $C_6D_4^+$.
[b]Equilibrium values.
[c]Assuming $B'-B''=C'-C''$.

Proof comes from a mass-selective matrix study that was performed following the gas phase analysis. This experiment combines mass selection and matrix isolation spectroscopy and has been described.[25] The $C_6H_4^+$ ($C_6D_4^+$) cations were produced from a phenylacetylene–deuterated-2,4-hexadiyne–) helium mixture in a hot cathode discharge source. A 90° deflector and a quadrupole mass spectrometer are used to steer the ion beam onto the matrix, where the mass-selected ions are codeposited with excess of neon at 6 K. The absorption spectra are recorded by guiding monochromatized light (0.1 nm bandpass) through the matrix onto a photomultiplier. The resulting spectra for matrices prepared with mass of $C_6H_4^+$ or $C_6D_4^+$ are shown in Fig. 4. Two strong bands are observed, one around 609 nm and one around 585 nm, for $C_6H_4^+$. No strong bands are observed to lower energy; i.e., the band at 609 nm corresponds to the origin band. The main structures to the blue of the dominant peaks (609 nm for $C_6H_4^+$ and 606 nm for $C_6D_4^+$) are matrix artifacts, site structure. The 114 cm^{-1} blueshift of the gas-phase spectrum with respect to the matrix band at 609 nm is typical for a chain of this size and in this frequency regime.[3] The band at 585 nm is due to another isomer of $C_6H_4^+$, since the relative intensity of the two bands varies strongly with different precursors. Upon deuteration the band at 609 nm shifts by 62(3) cm^{-1} to the blue—i.e., close to the 67 cm^{-1} shift observed in the gas phase upon deuteration. The band observed at 585 nm in the matrix only shifts 17(3) cm^{-1} upon deuteration. Subsequent neutralization of the trapped species by irradiation of the matrix with a medium-pressure mercury lamp leads to the disappearance of both bands. This confirms that the carrier of the 609 nm matrix and the 604 nm gas-phase carrier is a $C_6H_4^+$ cation, as was concluded from the gas-phase spectrum.

IV. ASTROPHYSICAL RELEVANCE

All the spectroscopic information is in favor of the identification of the band observed at 604 nm as due to the $^2A''-X\ ^2A''$ electronic origin band transition of the nonlinear

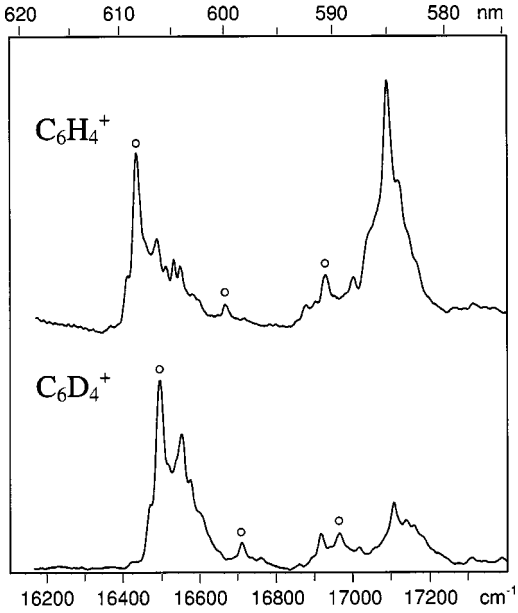

FIG. 4. Electronic absorption spectra of $C_6H_4^+$ (upper trace) and $C_6D_4^+$ (lower trace) measured in 6 K matrices after codeposition of mass-selected cations with excess of neon. The bands at 609 nm of $C_6H_4^+$ and at 606 nm of $C_6D_4^+$ correspond to the gas-phase spectra shown in Figs. 1 and 2. The weaker bands at 600 and 591 nm for $C_6H_4^+$ and 599 and 590 nm for $C_6D_4^+$ (indicated by ○) exhibit an identical chemical behavior as the 609 nm band on $C_6H_4^+$ and the 606 nm band on $C_6D_4^+$ and are due to transitions to vibrationally excited levels in the upper $^2A''$ state. The bands at 585.3 and 584.7 nm of $C_6H_4^+$ and $C_6D_4^+$ are due to another isomer.

planar $H-C\equiv C-C\equiv C-CH=CH_2^+$ carbon chain cation. The inferred rotational constants may guide a search for this species by millimeter-wave spectroscopy to allow a more accurate geometry determination. This is of interest as the number of microwave studies of carbon chain cations is still rather limited.[26] It furthermore would make a radio-astronomical search for this species in dense interstellar clouds possible. The optical spectrum obtained here allows a comparison with the available lists of diffuse interstellar band (DIB) positions.[27,28] A comparison with the hitherto reported DIBs shows that there exists an overlap between the band observed around 16 545 cm^{-1} and a broad DIB [full width at half maximum (FWHM) ~14 cm^{-1}] reported at 16 537.3 cm^{-1}. In order to check whether this discrepancy of 8 cm^{-1} might be due to a temperature effect, a comparison has been made between an artificial DIB spectrum in the 604 nm range and the $C_6H_4^+$ spectrum for low (10 K), intermediate (40 K), and high (150 K) temperatures (Fig. 5). Although it is clear that for higher temperatures the spectrum of the nonlinear $C_6H_4^+$ might start filling up the broadband around 16 545 cm^{-1}, it is hard to account for the difference in intensity of the *P* and *R* branches. This is not reflected in the DIB spectrum.

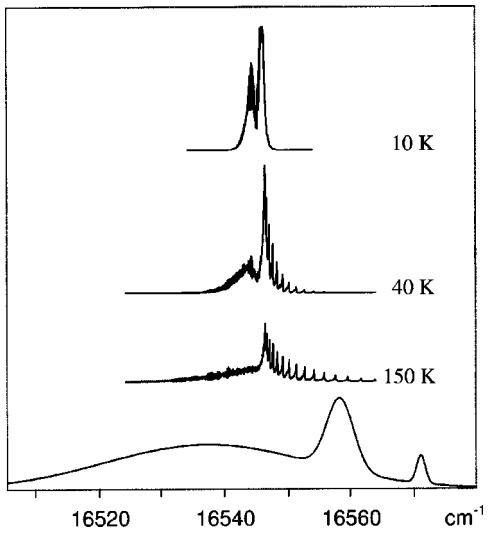

FIG. 5. Artificial DIB spectrum (Ref. 27) in the 604 nm range (lowest trace) and the simulated $C_6H_4^+$ spectra for 10, 40, and 150 K (upper three traces).

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